ON THE ASSIGNMENT OF VIBRATIONAL FREQUENCIES OF METHYL AND ETHYL BENZOATE

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ABSTRACT. The infra red spectra of methyl and ethyl benzoate in the liquid state and in solutions in $CHCl_3$ and CCl_4 and the Raman spectra of the compounds in the liquid state have been studied. Complete assignment of the observed frequencies to different modes of vibrations of the phenyl ring and the substituent groups has been proposed.

INTRODUCTION

The Raman spectra of methyl benzoate and ethyl benzoate were earlier studied by several authors (Ghosh and Kar, 1931; Matsuno *et al*, 1933; Kohlrausch *et al*, 1933; Murty *et al*, 1939; Herz *et al*, 1943; Hariharan, 1954; Puranik, 1955; Biswas, 1955) and tentative assignment for some of the frequencies was proposed by Hariharan (1954) and Puranik (1955). Later, Katritzky *et al*, (1960) studied a large number of ethyl and methyl esters other than benzoates and assigned most of the bands including those due to alkyl group to specific molecular vibrational modes. In continuation of previous work (Chattopadhyay *et al*, 1966; Chattapadhyay, 1967) on the vibrational spectra of substituted benzene compounds with large substituent group, the Raman spectra, the states of polarisation of the Raman lines and the infra red spectra of methyl and ethyl benzoate have been throughly investigated and an attempt has been made to present a complete assignment of the observed vibrational frequencies in the light of recent discussions on the characteristic phenyl ring frequencies (Whiffen, 1956; Green *et al*, 1961; Green, 1962; Stephenson *et al*, 1961) and the characteristic frequencies of carbonyl and alkyl groups (Bellamy, 1959; Sheppard *et al*, 1953; Katritzky *et al*, 1960).

EXPERIMENTAL

The samples were supplied by Fischer Scientific Company. The compounds were first fractionally distilled and in each case the proper fraction was collected and repeatedly distilled under reduced pressure before use. The infra red spectra of the two compounds in the liquid state and in dilute solutions in CCl_4 and $CHCl_3$ were recorded with a Perkin Elmer Model 21 spectrophotometer fitted

with NaCl optics. The Raman spectra and the character of polarisation of the Raman lines were studied in the manner described in a previous paper (Chattopadhyay *et al*, 1966).

RESULTS AND DISCUSSION

The Raman shifts and the infra red frequencies of the molecules of methyl and ethyl benzoate are given respectively in tables 1 and 2 and the assignments of the frequencies to vibrationl modes of the ring and the substituent groups are summarised in tables 3 and 4 respectively.

Table 1

Methyl benzoate

Raman shift (cm^{-1}) Liquid at 28°C	Infra red frequencies (cm^{-1})		
	Pure Liquid (Thin film) at 25°C	Solution in	
		CCl_4	$CHCl_3$
134 (1) D*			
175 (0)			
218 (5) D			
360 (4) P			
621 (6) D			
679 (2) P*	674 m	670 s	
	686 m	683 s	684 s
	710 vs	712 vs	710 vs b
808 (0)	808 vw	815 ws	
826 (6) P	824 m		
850 (0)	850 m	850 m	
942 **	938 w	935 w	930 s
969 (1)	966 m		
1003 (10) P	1004 w		
1028 (4) P	1030 s	1030 s	1028 s
1064 (2)	1074 s	1072 s	1072 s
1111 (3) P*	1114 vs	1114 vs	1115 vs
1160 (3) D	1162 m	1162 vs	
1183 (4) P	1181 s	1180 s	1178 s
	1258 m sh	1255 s	1252 s
1277 (8) P	1282 vs	1282 s	1285 v sb
1311 (3) P	1320 vs	1318 vs	1320 vs
1376 (0)			
1435 (1) P*			
1452 (2) D*	1458 vs	1458 s	1455 vs
1495 (2)	1498 m	1499 w	1500 m
1549 (1)			
1591 (1)			
1603 (10 D	1606 s	1606 m	1605 m
1722 (6) P	1725 vs	1730 vs	1720 vs
2851 (0)	2850 w		2846 vw
2951 (3) P	2956 m sh		
3073 (5b) P			

*Polarisation data taken from Biswas (1955)

**Frequency taken from Biswas (1955)

Table 2

Ethyl benzoate

Raman shift (cm^{-1}) Liquid at 28°C	Infra red frequencies (cm^{-1})		
	Pure Liquid (Thin film) at 25°C	Solution in	
		CCl_4	$CHCl_3$
185 (5b) D			
333 (4) P			
394 (1b)			
432 (0)			
492 (1)			
556 (0)			
620 (6) D			
675 (3)	674 m	674 m	
	686 m	685 m	685 m
	710 vs	709 vs	708 vs
787 (2)*	780 m		
811 (2)	808 m	808 vs	
848 (6) P	850 w		
954 (0)*			
	970 w sh	975 m	
985 (5)***			
1002 (10) P	1003 m	1002 m	1004 w
1028 (3) P	1030 vs	1030 vs	1030 m
	1072 vs	1070 s	1070 m
1105 (5) P	1110 vs	1110 vs	1110 vs
1162 (4) D	1160 m sh	1160 m sh	
1176 (2) P	1178 vs	1176 vs	1175 w
1191 (2)	1210 w	1212 m sh	
	1245 s sh	1254 vs	
1272 (6) P	1280 v sb	1275 vs	1285 vs
1305 (3) P	1318 vs	1316 m	1318 s
	1340 w sh	1342 w sh	
1372 (2)	1370 vs	1368 m	1368 s
1397 (1)	1396 m	1394 w	1394 s
1453 (3) D	1455 vs	1454 m	1454 m
	1480 m sh	1478 m sh	1468 m sh
1489 (2)	1495 w sh	1494 w sh	1495 w sh
	1590 m	1587 w	1588 w
1600 (8) D	1605 m	1604 w	1602 w
	1640 vw	1645 vvw	1645 w sh
1718 (6) P	1724 vsb	1722 vs	1716 vs
	2870 w sh	2868 w sh	
	2902 m sh		2905 vvw
	2920 m	2920 w sh	
2941 (3) P		2940 w sh	2935 w sh
2954 (4b) P**	2955 m		2960 w
2980 (2)	2970 m	2975 m sh	2974 w sh
	2998 s	2986 mb	2998 m
	3010 s sh	3008 m sh	
3072 (6b) P			
	3086 mb	3080 w sh	3086 m

*Frequency taken from Biswas (1955)

**Polarisation data taken from Biswas (1955)

***Frequency taken from Puranik (1955)

Table 3

Summary of assignments of the phenyl ring vibrations

Symmetry species under C_s point group and approx. nature of the mode	Correspondence with vibration No in benzene (Pitzer and Scott 1943)	Species under C_{2v} point group	Vibrational frequencies of C_5H_6X (in cm^{-1})	
			$X=COOCH_3$	$X=COOC_2H_5$
a′				
ν(CH)	20A	a_1		3086
ν(CH)	20B	b_1		3086
ν(CH)	2	a_1	3073	3072
ν(CH)	13	a_1	3073	3072
ν(CH)	7B	b_1	3073	3010
ν(CC)	8B	b_1	1603	1600
ν(CC)	8A	a_1	1591	1590
ν(CC)	19A	a_1	1495	1489
ν(CC)	19B	b_1	1452	1453
ν(CC)	14	b_1	1376	1372
β(CH)	3	b_1	1311	1305
β(CH)	9A	a_1	1183	1176
β(CH)	9B	b_1	1160	1162
β(CH)	15	b_1	1064	1072
β(CH)	18A	a_1	1028	1028
Ring	1	a_1	1003	1002
α(CCC)	6B	b_1	621	620
X-sensitive	7A	a_1	1111	1105
X-sensitive	12	a_1	826	848
X-sensitive	6A	a_1	360	333
X-sensitive	18B	b_1	218	186
a″				
γ(CH)	5	b_2	969	970
γ(CH)	17A	a_2	942	954
γ(CH)	10A	a_2	850	
γ(CH)	11	b_2	710	710
γ(CH)	17B	b_2	686	686
φ(CC)	4	b_2	679	675
φ(CC)	16A	a_2		432
X-sensitive	16B	b_2		394
X-sensitive	10B	b_2	134	

Table 4

Summary of assignments of internal vibrations of substituent groups

Approximate nature of the modes	Methyl benzoate	Ethyl benzoate
*CH_2 asymmetric stretching		2970 ?
CH_3 asymmetric stretching	2951	2954
*CH_2 symmetric stretching		2902
CH_3 symmetric stretching	2850	2870
C=0 bond stretching	1722	1718
CH_3 asymmetric bending	1435	1480
*CH_2 scissoring		?
CH_3 symmetric bending		1397
C-O bond stretching	1277	1272
*CH_2 wagging		1254
**OCH_3 rocking	1258	
*CH_2 twisting		1191
C-C stretch		985
CH_3 out-of-plane rocking	808	811
*CH_2 rocking		787

*Vibrational mode of the CH_2 group in ethyl benzoate only
**Mode in methyl benzoate only.

I. *Assignment of vibrations of the phenyl ring*

The molecules of methyl benzoate and ethyl benzoate possess only one symmetry element, namely, the element of identity and would give rise to forty eight and fifty seven modes and frequencies of vibration respectively. In assigning these vibrational frequencies to different modes of the constituent parts of the molecules, the whole of the substituent group may be, in a first approximation, treated as a single unit X. Then the C_6H_5X molecule will give rise to thirty vibrations characteristic of the phenyl ring and the additional modes will be derived from the internal vibrations of the substituents. Now the C_6H_5X molecule may be considered to belong to the C_{2v} point group and the thirty vibrations will be distributed over the four different species as $11a_1+10b_1+6b_2+3a_2$. Of these all, except the a_2 mode which is inactive in the infra red, will be allowed in both the Raman and infra red spectra, only the $a_1$mode giving rise to polarised Raman lines.

In the second approximation if the vibrations of the alkyl groups are treated independently and completely separately, then considering only the part O = C—O of the substituent group attached to a carbon atom of the phenyl ring, the molecules may be assumed to belong to the point group C_s, the plane of the phenyl ring being the plane of symmetry. Under such condition this part of the molecule, in each case, will give rise to thirty six vibrations and if the internal vibrations of O = C—O group are disregarded the thirty characteristic phenyl ring vibrations under C_s will be divided into $21a'+9a''$ modes. It will be, however, helpful to note that the $21a'$ vibrations of the C_s symmetry may be derived from the $11a_1+10b_1$ modes and the $9a''$ vibrations from the $6b_2+3a_2$ modes of the C_{2v} symmetry because the Raman and the infra red activity and polarisation character of some of these vibrations may be expected to be largely determined by the symmetry of the phenyl ring which is C_{2v} for the C_6H_5X molecule.

It may be noted that in each of the molecules besides the thirty vibrational frequencies characterising the phenyl ring modes there will be at least six more characteristic vibrational frequencies arising from the modes in O = C—O, some of which will be easily recognised. Finally, as indicated above, the remaining vibrational modes, twleve for methyl benzoate and twenty one for the ethyl ester, of the alkyl group which are attached to the nuclei through the C—O bond of the O = C—O group, may be treated independently of those of the phenyl ring. Since the methyl group corresponds to a higher symmetry group C_{3v} some of the modes will be degenerate and will not give rise to separate vibrational frequencies, as a result of which the number of observed frequencies will be smaller than the number of modes. The assignments with relevant discussion are presented in the following paragraphs.

(a) *Methyl benzoate*

The six carbon stretching frequencies are derived from the modes 8, 9, 14 and 1 of benzene (Wilson, 1934; Pitzer and Scott, 1943). The degenerate mode 8 will be split up into two components and these can be reasonably identified with the Raman shifts 1591(8A) and 1603 cm^{-1}(8B) respectively. Similarly, the Raman lines at 1452 and 1495 cm^{-1} have been assigned to components 19B and 19A of the mode 19 respectively. For C_{2v} point group, the modes 8B and 19B will give rise to vibration of type b_1 which will be depolarised in Raman effect. The observed depolarisation of the Raman lines at 1603 and 1452 cm^{-1} probably indicates that these essentially phenyl ring vibrations retain the b_1 character of the mode in the C_{2v} symmetry of the ring. The strong and polarised Raman line at 1003 cm^{-1} has been assigned to the ring breathing mode. The corresponding infra red band at 1004 cm^{-1} is weak. This may be explained by the fact that this vibration is essentially unchanged from the infra red inactive a_{1g} mode in benzene itself. The other carbon stretching mode corresponding to the mode 14 in benzene gives rise to the frequency 1376 cm^{-1}.

Of the six carbon bending vibrations arising out of the modes 4, 6, 12 and 16, the modes 6A, 12 and 16B are sensitive to substitution(Whiffen, 1956; Green, 1962). The strong polarised line at 826 cm^{-1} is assigned to the mode 12 belonging to a' class in C_s symmetry. The strong depolarised Raman line at 621 cm^{-1} can be assigned to one of the components (6B) of the mode 6 which becomes a vibration of b_1 class for C_{2v} symmetry, the other X-sensitive component 6A (a_1 for C_{2v} symmetry) being identified with the polarised Raman line at 360 cm^{-1}. The a'' vibration corresponding to the mode 4 is placed at 679 cm^{-1}. The frequencies due to the two components of mode 16 could not be observed in the case of methyl benzoate.

The four modes 2, 7, 13 and 20 are responsible for the six C-H stretching vibrations of the phenyl ring. The strong and polarised Raman line at 3073 cm^{-1} may justifiably be attributed to the a' vibration corresponding to mode 2. The a' components of the degenerate modes 7 and 20 could not be detected probably because they are superimposed on the broad band at 3073 cm^{-1} and are not resolved from each other. This may also be the case with mode 13. There is apparently some uncertainity regarding the assignment of the X-sensitive stretching mode. Following Whiffen (1966), Stephenson *et al* (1961) assigned the bands in the region 1050-1250 cm^{-1} to mode 20A for monosubstituted benzene compounds while Green *et al* (1961) assigned bands in this region to mode 7A treating the latter as the X-sensitive mode. Incidentally, in molecules with C_s symmetry both 20A and 7A will give rise to polarised Raman lines of a' class. In table 1, the line at 1111 cm^{-1} which is polarised in Raman effect has been tentatively assigned to mode 7A.

The degenerate in-plane CH deformation mode 9 splits up into two vibrations, the frequencies being readily assigned at 1183(9A) and 1160 cm^{-1}(9B) respectively. The X-insensitive component of 18 is at 1028 cm^{-1} and the X-sensitive component of the same is at 218 cm^{-1}. The polarisation data conform to C_{2v} symmetry of the ring of the C_6H_5X molecule. Of the two remaining deformation vibrational modes 15 and 3, the former is identified with the band at 1064 cm^{-1} and the latter with that at 1311 cm^{-1}.

The out-of-plane CH deformation vibrations of a'' class arising from the modes 5 and 17B have been assigned at 969 and 686 cm^{-1} respectively. In the case of both the esters the infra red spectrum shows a strong band at 710 cm^{-1} while the Raman spectrum does not show any corresponding frequency shift. Jones and Sandorfy (1956) reviewed the results of various authors and noted that monosubstituted benzene compounds exhibit strong infra red band in the 730 cm^{-1} region, the corresponding Raman shift being absent. This band was attributed to out-of-plane C-H deformation vibration corresponding to a_{2u} mode 11 in benzene. According to Whiffen and others the average position of this band in monosubstituted benzenes is at about 750 cm^{-1}. The strong infra red band at 710 cm^{-1}

has therefore been assigned to this vibration which is probably not essentially different from the corresponding a_{2u} mode in benzene. The lowest frequency corresponding to the X-sensitive mode 10B has been placed at 134 cm^{-1} following the general behaviour of this mode in monosubstituted benzenes. The modes 17A and 10*A* can be recognised in the Raman lines at 942 cm^{-1} and 850 cm^{-1}, the intensity of the corresponding infra red bands being very weak. This fact appears to indicate that the vibrations are mostly unchanged from the infra red inactive a_2 modes of C_6H_5X molecules.

(b) *Ethyl benzoate* :

In the case of ethyl benzoate, the phenyl ring vibrations can be readily assigned by comparing its spectrum with that due to methyl benzoate. Such a comparison shows that in ethyl benzoate there are two Raman lines at 432 and 394 cm^{-1} attributed to the modes 16A and 16B which are not observed in methyl benzoate. Further in ethyl benzoate the band at 3086 cm^{-1} due to mode 20A observed in the infrared is resolved from that at 3072 cm^{-1}. Moreover there is a strong infrared band band at 3010 cm^{-1} appearing as shoulder in ethyl Benzoate which can be assigned to the mode 7B of benzene.

II. *Internal vibrations of the substituent groups*

The assignments of vibrations of substituent groups have been made on the basis of results discussed by previous authors (Sheppard and Simpson, 1953; Brown *et al*, 1950; Brown and Sheppard, 1950; Katritzky *et al*, 1960; Wilmshurst, 1957). As indicated in table 4, the C-H stretching and bending modes can be reasonably associated with some of the bands in the 2800-3000 cm^{-1} and 1200-1500 cm^{-1} regions, though overlapping of phenyl ring C-H vibrations and their overtones makes the assignments somewhat tentative. The CH_2 scissoring vibrational frequency which usually falls in the 1450-1500 cm^{-1} region could not be definitely identified. The characteristic C=O and C—O streching vibrations can be readily identified with the bands at 1722 and 1277 cm^{-1} in methyl benzoate and those at 1718 and 1272 cm^{-1} in ethyl benzoate, respectively. In methyl benzoate, OCH_3 rocking frequency has been assigned at 1258 cm^{-1} (Wilmshurst, 1957) and in ethyl benzoate the methylene wagging is at 1254 cm^{-1}. The methylene twisting mode which is generally weak or absent in infra red usually occurs at lower frequencies than does the wagging mode and has been reported over a wide frequency range in the 1095-1300 cm^{-1} region (Sheppard and Simpson, 1953; Brown *et al*, 1950; Brown and Shepperd, 1950). The Raman line at 1191 cm^{-1} which is present only in the ethyl ester has been attributed to this mode. In support of this it may be noted that the corresponding infra red band is very weak. In addition to these vibrations, several skeletal bending and torsional vibrations of C-C bond may be expected to occur possibly at lower frequencies and some of

the observed Raman lines of lower frequency shifts may be associated with such motions. It is, however, difficult to characterise these modes definitely.

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